FEASIBILITY STUDY: ANALYSIS OF AQUEOUS POLYMER ADDITIVES USING CYLINDRICAL INTERNAL REFLECTANCE SPECTROSCOPY

FINAL REPORT

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SUMMARY

This report incorporates the contents of an interim submission made in April 1985.
Additional material is confined to description of the lack of feasibility of an alternative "concentration-enhancing" technique, a literature review, and description of a modification to the CIRCLE cell allowing its use for the monitoring of real-time reactions under conditions of elevated temperatures and/or pressures (this modification was made after completion of the contracted work).

It is suggested that the incorporation of the CIRCLE cell into a pressure reactor has the promise of increasing the utility of this technique in fossil-fuel studies.
An account of the design of the modification is being given at the 69th Conference of the Chemical Institute of Canada, Saskatoon, June 1986.

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Feasibility Study:

Analysis of Aqueous Polymer Additives using Cylindrical Internal Reflectance Spectroscopy

INTERIM REPORT

Submitted by: Brian M. Lynch, Principal Investigator

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Experimental Procedures

CIRIFT spectra were acquired with the Bruker IFS110 Spectrometer using the "Open-Boat" CIRCLE cell with ZnSe cylindrical element (the cell was modified by provision of stainless-steel covers) and the standard DTGS detector. Trapezoidal apodization was employed. The interferometer mirror velocity was 0.118 cm s^{-1} (velocity setting "4"). Acquisitions of 256 scans at 8 cm^{-1} resolution (spectral encoding every 4 cm^{-1}) were made for each of the following:

(a) File AFC

single-beam spectrum of the empty cell (signal corresponds to absorptions through the optical path of the instrument)

(b) File AFB

single-beam spectrum of a standard "reference" sample of deionized pure water

(c) File AFA

single-beam spectrum of aqueous solution under examination

These files were manipulated using the software command SSA (subtract spectrum automatically), which calculates the quantity

Absorbance Subtraction Spectrum = -log (AFA/AFC) - CON <-log (AFB/AFC)>

where the subtractive constant "CON" is established by a least-squares procedure.

This command displays the two absorbance spectra and the absorbance subtraction spectrum corresponding to the solute species.

The absorbance subtraction spectrum is then saved via a specified ART (arithmetic) command and plotted onto a permanent file.

Generally, portions of the complete spectral files for the analytical frequency ranges were used for the generation of the absorbance subtraction curves. The frequency ranges used corresponded to "windows" where absorptions due to water were not significant.

Alternative manipulations are successful at high solute concentrations (2-5 % by weight), but the above procedure provides the maximum sensitivity.

CIRIFT spectra were acquired for a series of concentrations of aqueous solutions of the following solute species:

1. Praestol 444K Surfactant, 100 % cationic species
2. Praestol 2900 Surfactant, 25 % anionic species
3. Poly(acrylic acid), Aldrich 18,128-5
4. Tetrabutylammonium hydrogen sulfate, ICN Pharmaceuticals Lot 30018-A

Attempts were made to obtain definitive spectra of a range of other surfactant species supplied by CRL Edmonton, but diagnostic absorption bands were not sufficiently intense to provide satisfactory composition vs. absorbance plots.

Results

1. Praestol 444K Surfactant

Figure 1 displays a CIRIFT spectrum acquired using the above absorbance-subtraction procedure, for a 2 % aqueous solution, together with the PAIFT spectrum of the solid sample. The "window" region from 1250-1100 cm^{-1} was selected for analysis; the more intense features from 1700-1400 cm^{-1} are subject to errors in the subtraction procedure as a result of the intense water absorptions.

The integrated absorbance between 1250-1100 cm^{-1} (normalized to unity at the highest concentration used, 20000 ppm (2.0 %)) was a good linear function of concentration in the range 2000-20000 ppm (0.2-2.0 %), as shown in Table 1 and illustrated graphically in Figure 2.

The apparent detection limit at which significant confidence could be assigned to an observed "absorbance subtraction" peak is 1000 ppm (0.1 %).

This could possibly be improved through use of an MCT detector, not available to us, but installed in the Edmonton CRL instrument.

The detection limit for this solute may be lowered by allowing the solvent to evaporate from the surface of the ZnSe element of the CIRCLE cell. Figure 3 illustrates this for the film obtained by evaporation of the 0.2 % solution (again compared with the PAIFT spectrum), and Figure 4 for the film from a 0.01 % solution (100 ppm).

2. Praestol 2900 Surfactant (25 % anionic)

Figure 5 shows an "inverse transmission" spectrum (i.e. AFB/AFA) for 1.8 % aqueous Praestol 2900, and the corresponding PAIFT spectrum. Unlike the cationic surfactant species, there are significant differences between the solution and the solid-phase spectra. The best region for analysis was between 1200-1100 cm^{-1}, and the peak absorbance at 1115 cm^{-1} was selected, and in Table 2 the absorbances are listed as a function of concentration in the range 1500-18000 ppm (0.15-1.8 %); the data fit a polynomial (mixed first and second degree curve) over this range, illustrated in Figure 6. Again, the detectability limit may be lowered by evaporation of the solvent, as illustrated in Figure 7 for a film evaporated from the 1500 ppm solution. Note that the evaporated film closely resembles the solid-phase spectrum.

3. Poly(acrylic acid)

This species possesses an intensely absorbing carboxylic acid group, possibly interacting strongly with the crystal surface. Thus it should be possible to use the peak absorbance of the carbonyl feature in the 1800-1600 cm^{-1} interval, even though water absorbs strongly in this region. Thus the peak absorbance (at approximately 1680 cm^{-1}) for the carboxyl group is readily detectable (see Figure 8, which compares the CIRIFT spectrum of a 2.5 % (25000 ppm) aqueous solution and the PAIFT spectrum), and the absorbance varies smoothly with concentration in the range 100 ppm to 10000 ppm (see Table 3 and Figure 9).

4. Tetrabutylammonium hydrogen sulfate

For this species, a diagnostic absorption centered at 1107 cm^{-1} appears in the CIRIFT spectra (aqueous solutions); this is not present in the solid-phase spectrum (compare Figure 10). The sensitivity of detection of this feature (assigned to S-O stretching frequencies) is such that it is discernable at 20 ppm of solute (approximately 6 ppm of sulfate species). The parameters of the polynomial relationship are listed in Table 4, and illustrated in Figure 11.

Preliminary Conclusions

It is possible to use Circular Internal Reflectance Infrared Fourier Transform (CIRIFT) spectroscopy to detect and quantitate the surfactant species Praestol 444K and Praestol 2900 at bulk concentrations of 1000 ppm and above.

Intensely absorbing chromophores (such as carboxyl or bisulfate/sulfate are detectable and quantifiable in the range 20 ppm - 6 ppm.

The detection limits for surfactant solutions may be lowered by evaporation of solutions to provide films on the CIRCLE cell surface.

The detection limits obtained from these experiments using a conventional (DTGS) detector are significantly below those claimed by the manufacturer (Barnes Analytical) for tests with the more sensitive MCT detector. Such a detector would presumably allow much better performance.

SURFACTANT PRAESTOL 444K. 100% CATIONIC

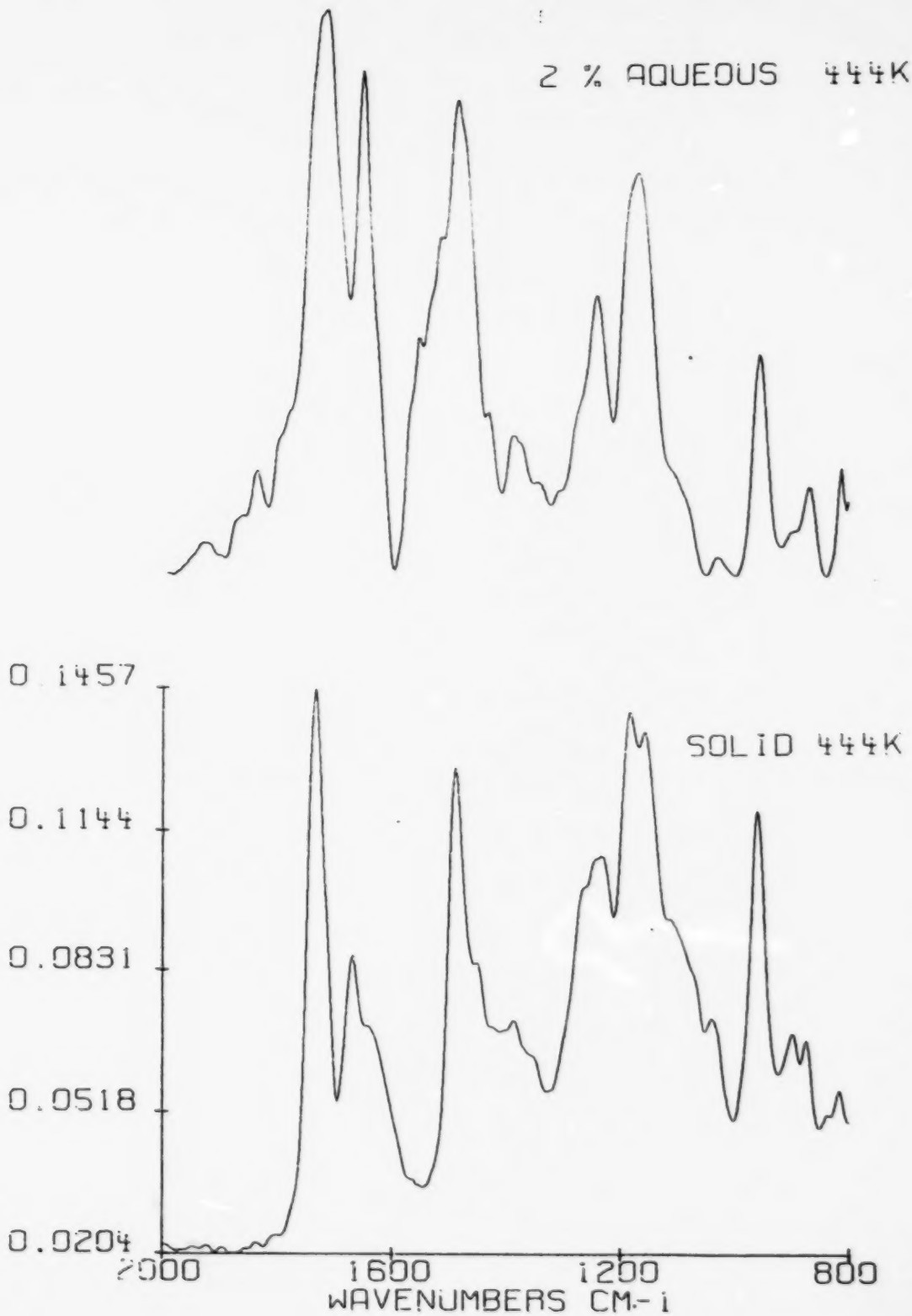
2 % AQUEOUS 444K
SOLID 444K
0.1457
0.1144
0.0831
0.0518
0.0204
2000
1600
1200
800
WAVENUMBERS CM-1

Figure 1

PARAMETERS OF LINEAR LEAST-SQUARES RELATIONSHIP
LINKING INTEGRATED ABSORBANCE AND CONCENTRATION (P.P.M.)
FOR AQUEOUS PRAESTOL 444K

y = normalized absorbance
x = concentration in p.p.m.

$y = 0.0348 + 0.0000490\ x$
$r = 0.996$
standard error of estimate = 0.033

Data

x	observed y (predicted y)
2000	0.1342(0.1329)
3000	0.1730(0.1818)
4000	0.1867(0.2308)
5000	0.3137(0.2800)
10000	0.5568(0.5247)
20000	1.0000(1.0145)

Table 1

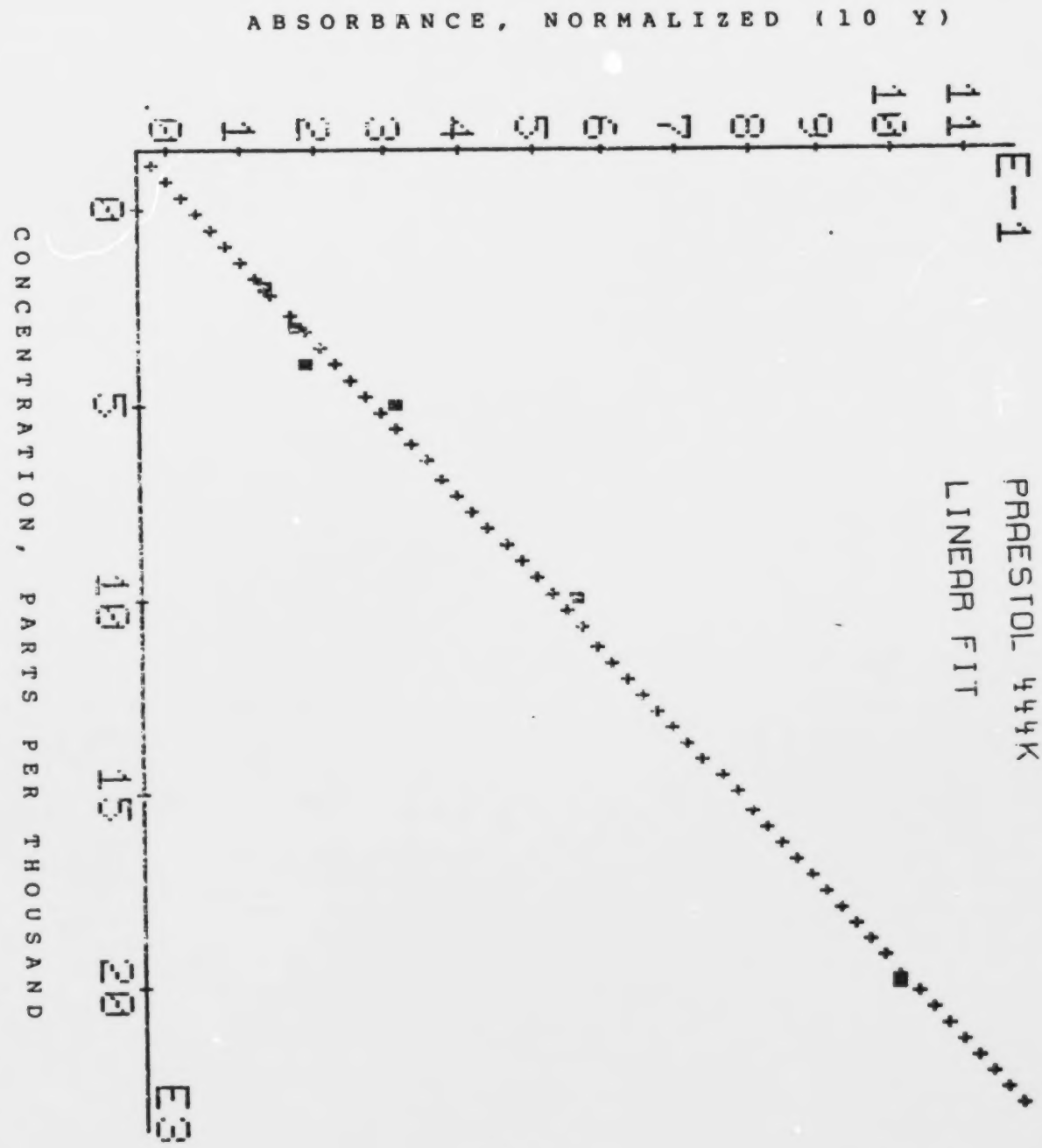
ABSORBANCE, NORMALIZED (10 Y)
0 1 2 3 4 5 6 7 8 9 10 11
E-1
PRAESTOL 444K
LINEAR FIT
0 5 10 15 20
E0
CONCENTRATION, PARTS PER THOUSAND

Figure 2

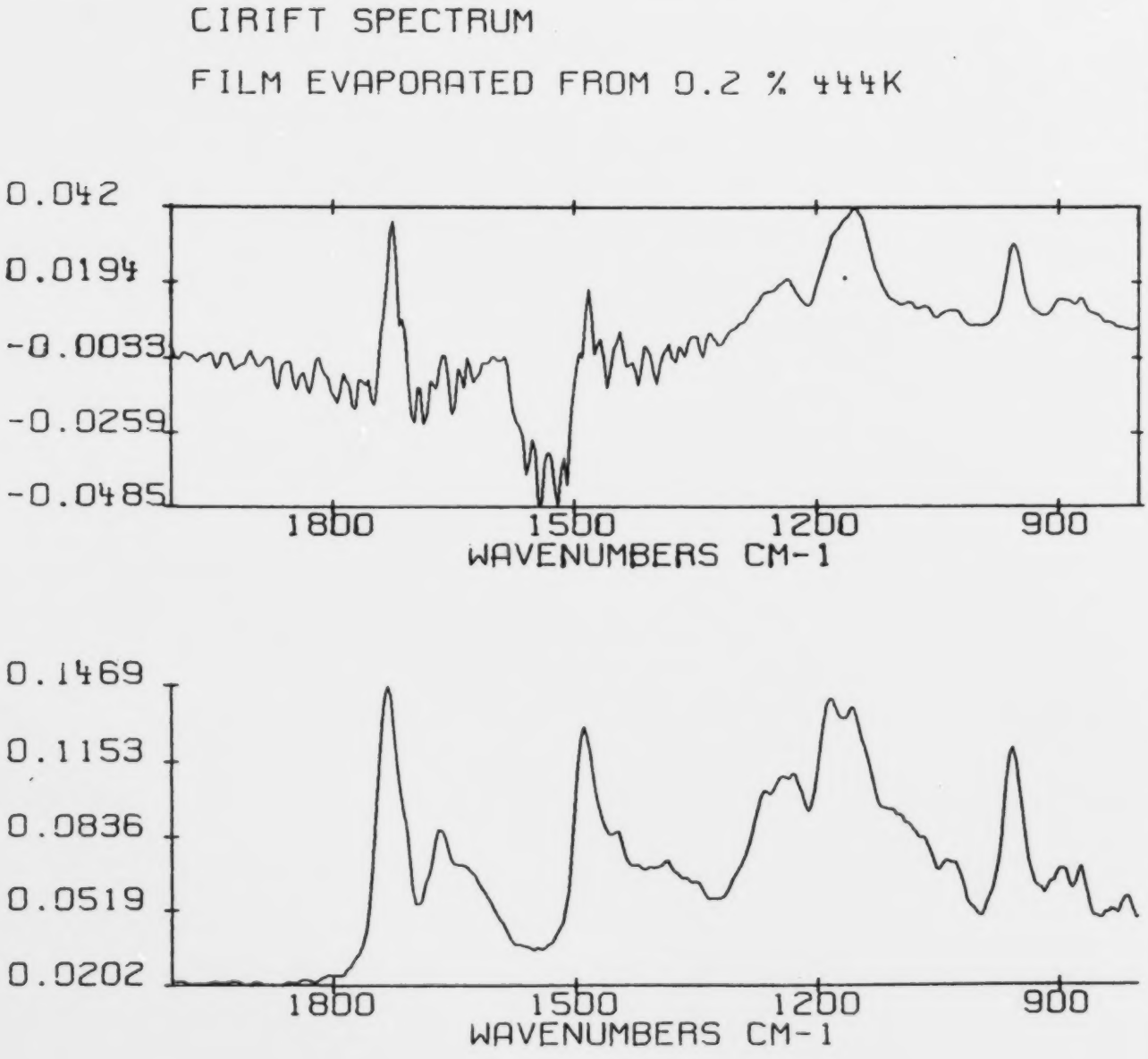
CIRIFT SPECTRUM
FILM EVAPORATED FROM 0.2 % 444K
0.042
0.0194
-0.0033
-0.0259
-0.0485
1800
1500
1200
900
WAVENUMBERS CM-1
0.1469
0.1153
0.0836
0.0519
0.0202
1800
1500
1200
900
WAVENUMBERS CM-1
PAIFT SPECTRUM 444K SOLID

Figure 3

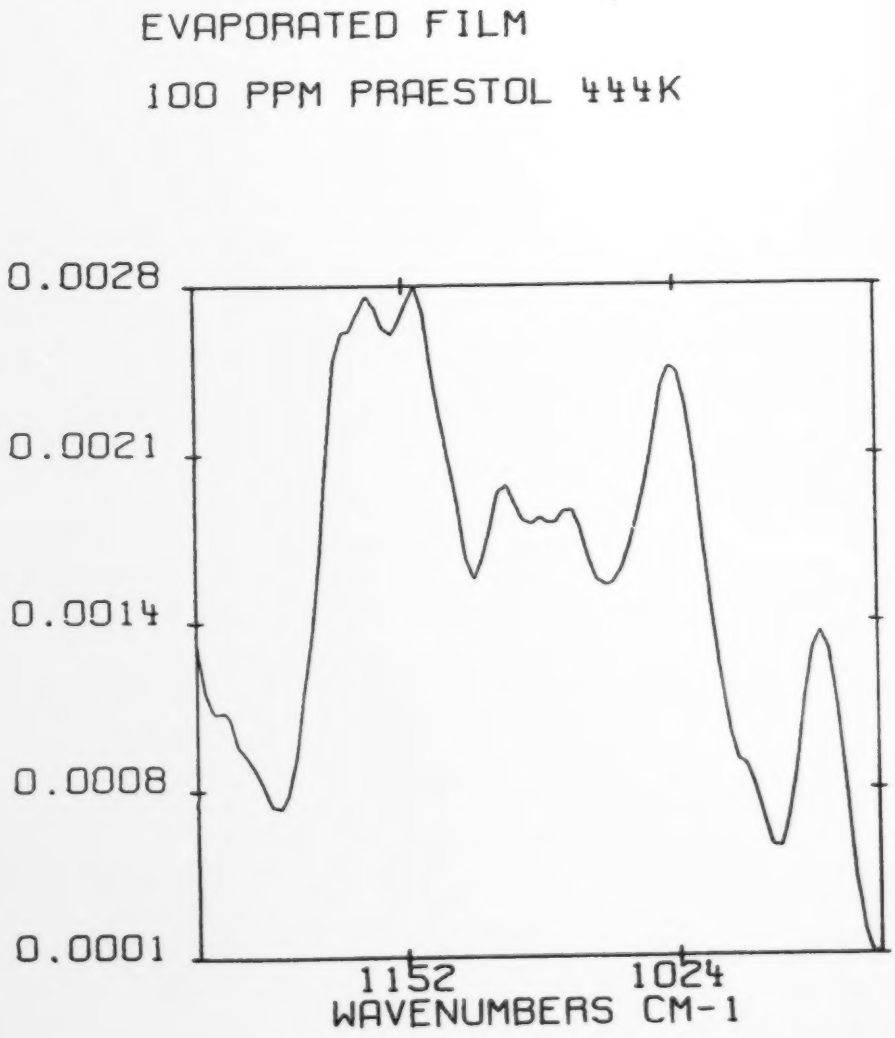
EVAPORATED FILM
100 PPM PRAESTOL 444K
0.0028
0.0021
0.0014
0.0008
0.0001
1152
1024
WAVENUMBERS CM-1

Figure 4

PRAESTOL 2900 25% ANIONIC

TOP - CIRIFT INVERSE TRANSMISSION
1.8 % PRAESTOL 2900 IN WATER
BOTTOM - PAIFT OF PRAESTOL 2900

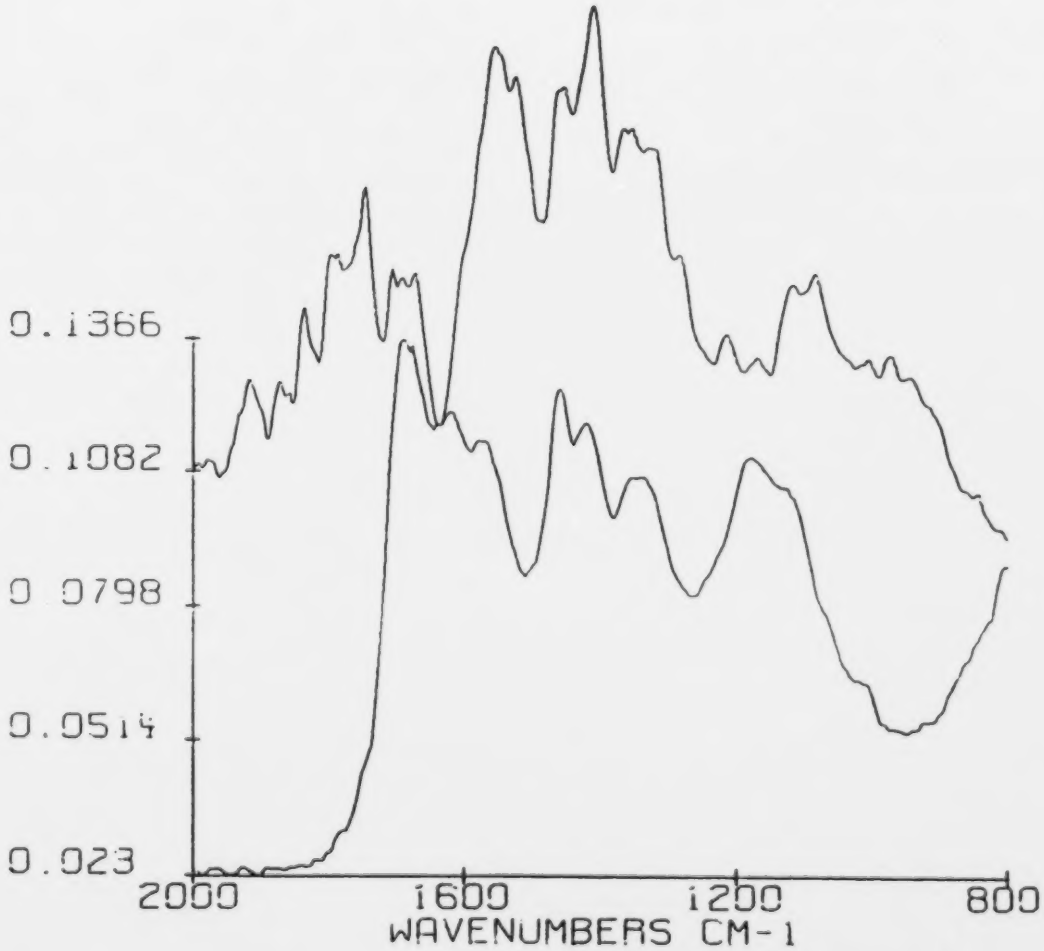

Figure 5

PARAMETERS OF POLYNOMIAL RELATIONSHIP LINKING PEAK ABSORBANCE AT 1115 $cm.^{-1}$ IN AQUEOUS PRAESTOL 2900 SURFACTANT WITH CONCENTRATION

y = 10000 x absorbance

x = concentration (p.p.m.)

$y = 3.171 + 0.0068\ x - 1.66 \times 10^{-7}\ x^2$

r = 0.987, n = 5

standard error of estimate = 5.57

Data

x	y observed (y predicted)
1500	10(13)
3000	28(22)
6000	34(38)
10000	56(55)
18000	72(72)

Table 2

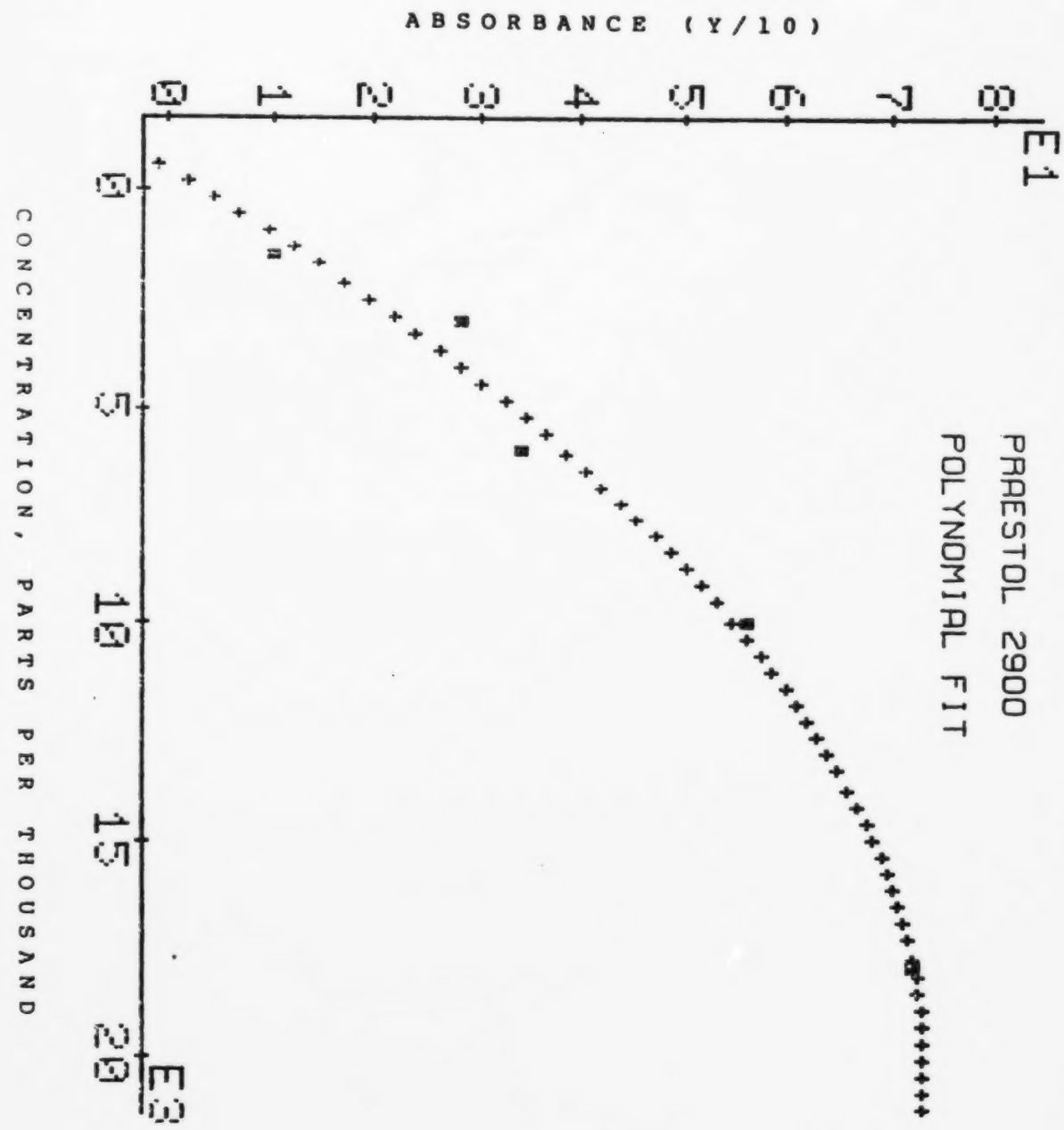
ABSORBANCE (Y/10)
0
1
2
3
4
5
6
7
8
E1
0
5
10
15
20
E0
CONCENTRATION, PARTS PER THOUSAND
PRAESTOL 2900
POLYNOMIAL FIT

Figure 6

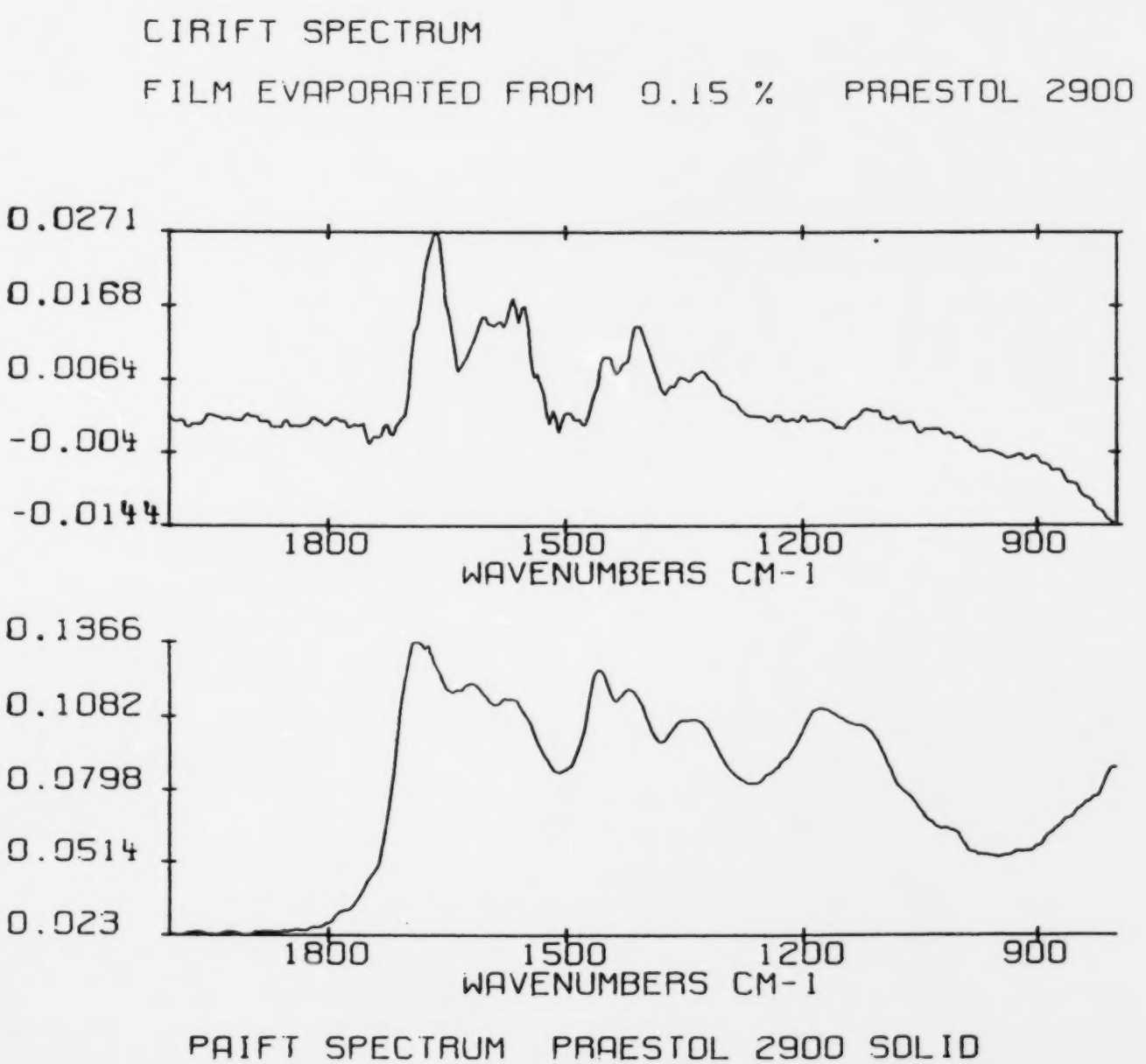
CIRIFT SPECTRUM
FILM EVAPORATED FROM 0.15 % PRAESTOL 2900
0.0271
0.0168
0.0064
-0.004
-0.0144
1800
1500
1200
900
WAVENUMBERS CM-1
0.1366
0.1082
0.0798
0.0514
0.023
1800
1500
1200
900
WAVENUMBERS CM-1
PAIFT SPECTRUM PRAESTOL 2900 SOLID

Figure 7

POLYACRYLIC ACID

TOP - 2.5 % AQUEOUS POLY(ACRYLIC ACID)
CIRIFT SPECTRUM
BOTTOM - PAIFT SPECTRUM. POLY(ACRYLIC ACID)

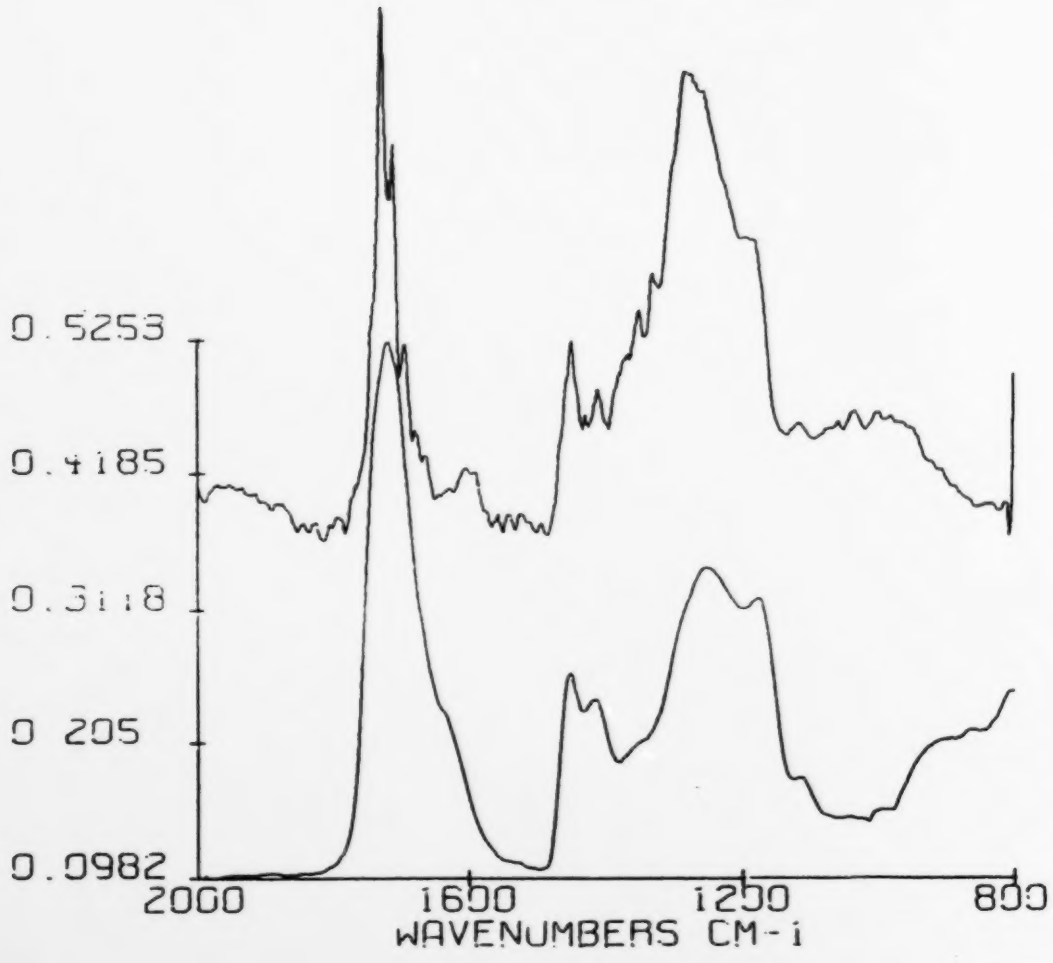

Figure 8

PARAMETERS OF POLYNOMIAL RELATIONSHIP LINKING ABSORBANCE OF CARBOXYL GROUP IN AQUEOUS POLY(ACRYLIC ACID) WITH CONCENTRATION

y = 10000x absorbance

x = concentration (p.p.m.)

$y = 294.19 + 0.321\ x - 1.56 \times 10^{-5}\ x^2$

r = 0.986, n = 18

standard error of estimate = 75.7

Data

x	y observed (y predicted)
100	329(326)
200	379(358)
300	413(389)
400	463(420)
500	478(451)
600	538(481)
700	539(511)
800	564(541)
900	570(571)
1200	636(657)
1300	684(685)
1400	698(713)
1600	684(768)
1800	697(822)
2000	709(874)
2500	1069(1000)
5000	1657(1510)
10000	1917(1945)

Table 3

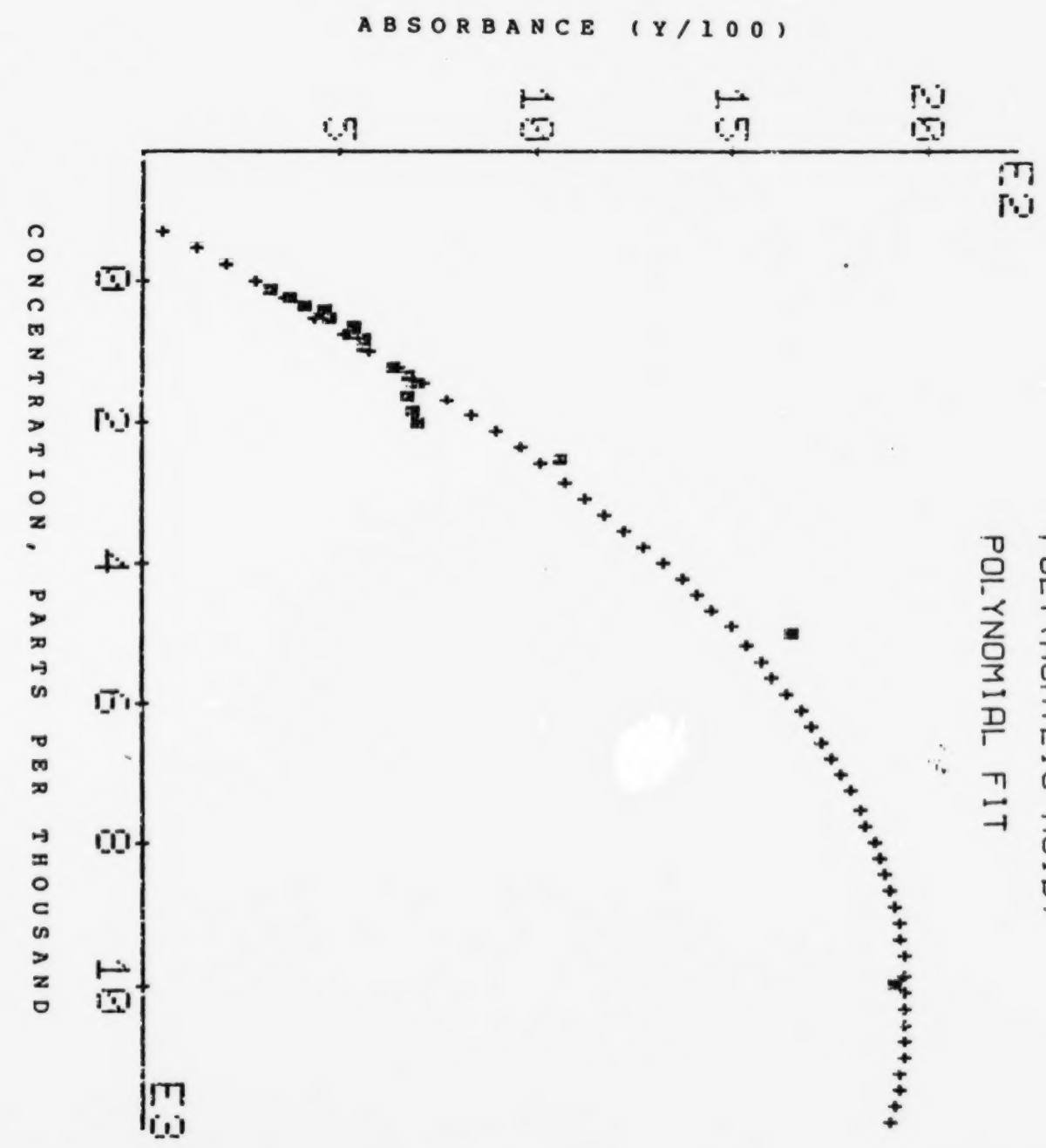
POLY(ACRYLIC ACID)
POLYNOMIAL FIT
ABSORBANCE (Y/100)
5
10
15
20
E2
0
2
4
6
8
10
E0
CONCENTRATION, PARTS PER THOUSAND

Figure 9

TETRABUTYLAMMONIUM BISULFATE

TOP - CIRIFT INVERSE TRANSMISSION

0.5 % BU4N+ HSO4- IN WATER

BOTTOM - PAIFT OF BU4N+ HSO4-

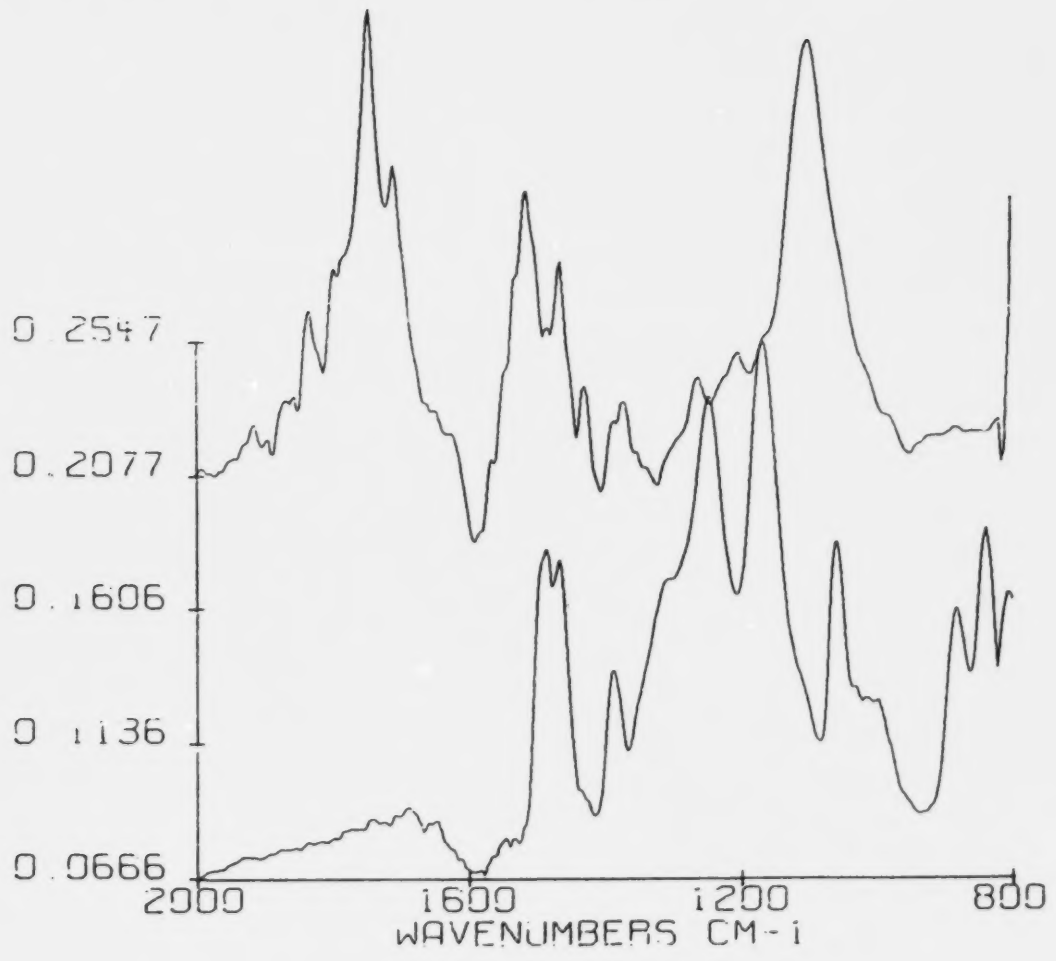

Figure 10

PARAMETERS OF POLYNOMIAL RELATIONSHIP LINKING ABSORBANCE OF SULFATE GROUP IN AQUEOUS TETRABUTYLAMMONIUM HYDROGEN SULFATE WITH CONCENTRATION

$y = 10000 \times \text{absorbance}$

$x = \text{concentration (p.p.m.)}$

$y = 43.11 + 0.060\,x - 6.16 \times 10^{-6}\,x^2$

$r = 0.996,\ n = 10$

standard error of estimate = 6.35

Data

x	y observed (y predicted)
20	33(44)
50	47(46)
100	52(49)
200	58(55)
500	72(72)
1000	106(97)
2000	138(139)
3000	161(168)
4000	187(185)
5000	191(190)

Table 4

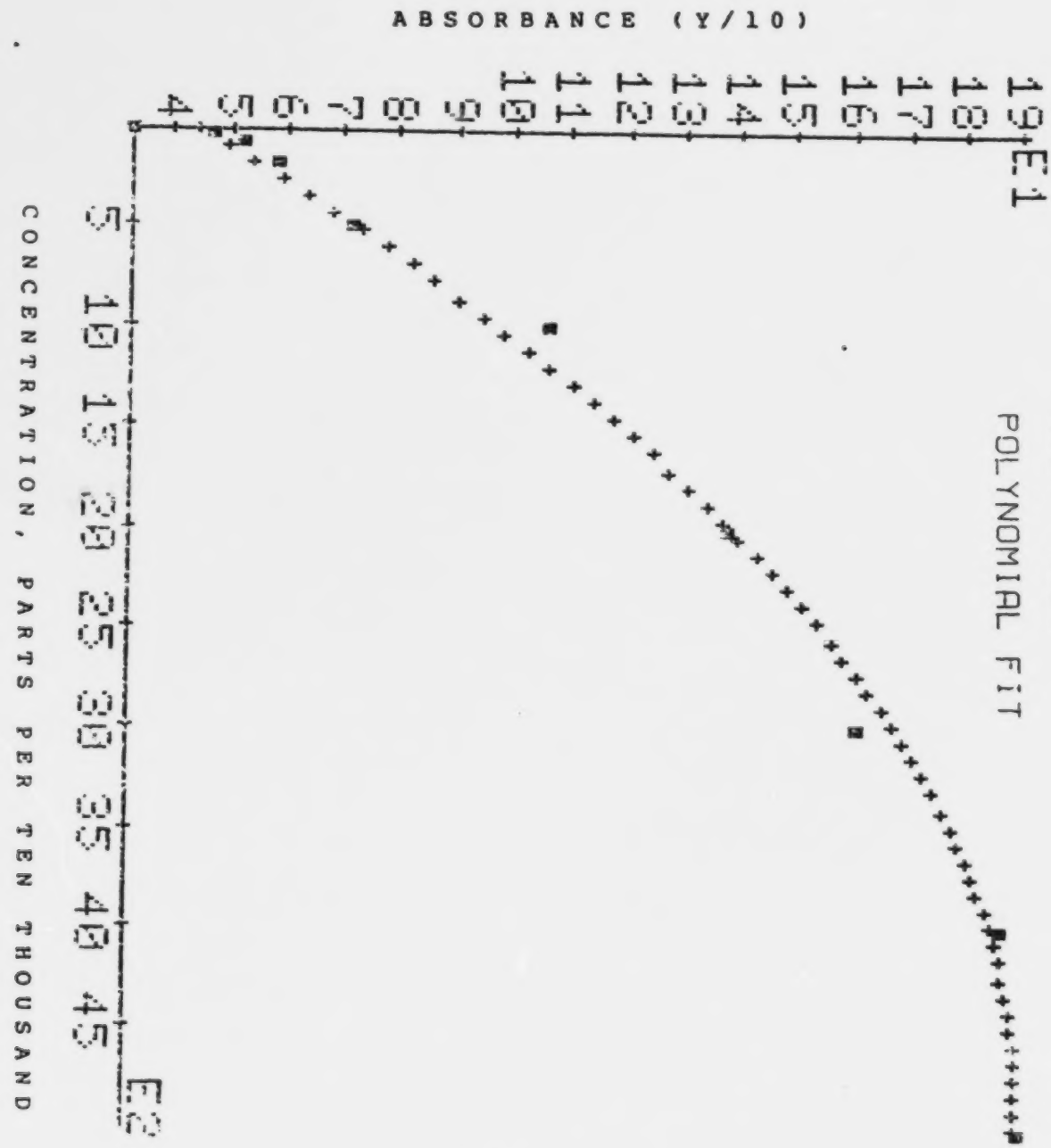
ABSORBANCE (Y/10)
1.9E1
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
NBU4+ HSO4-
POLYNOMIAL FIT
5 10 15 20 25 30 35 40 45
E2
CONCENTRATION, PARTS PER TEN THOUSAND

Figure 11

APPENDIX

Supplementary Discussion and Interpretation

Use of a Germanium Transmitting Element

The originally formulated "Statement of Work" for this research contract proposed that surface concentrations of the analyte species under examination might be enhanced through use of electrically charged transmission elements, composed of germanium and/or surface-oxidized germanium.

In a series of experiments along the lines of those in the body of this report (where a zinc selenide element was employed), but using a germanium rod as the transmission element, the detection limits for surfactant species were at least an order of magnitude higher.

Thus even if surface concentrations could be enhanced by charging the germanium surface, we would end up no better off. In effect, we would end up where we start off with the zinc selenide system.

The reason for the marginal performance of the germanium cylinder is simply that the transmission of mid-infrared radiation through the germanium element is about 20% that for a zinc selenide element, and the effective cut-off frequency is around 900 cm.-1

Our conclusion is that there is no point in proceeding with the "charging" approach unless some different transmitting element is employed.

The Nature of the Analyzed Surfactant Species

After completion of the experimental work, we learned the approximate nature of the functionalities present in these entities. The monomeric parent of the cationic constituent (e.g. in Praestol 444K) is this moiety:

(CH3.)3.N+.CH2.CH2.O.CO.CH:CH2

((trimethylammonio)ethyl acrylate)

and the diagnostic analytical region which was used (between 1250 & 1100 cm.-1) will have a major contribution from the C-O single bond frequency of the carboxylic ester component. As an alternative, the high-frequency carbonyl absorption (above 1750 cm.-1) might have been used.

In the anionic species, the monomeric parent is:

Na+ CH2:CH.CO.O-

(sodium acrylate).

Since the Beer-Lambert law was not followed for the anionic surfactant species, in a similar manner to poly(acrylic) acid, the carboxylic acid - carboxylate ion equilibrium distribution at the surface of the cylindrical element could be varying with bulk concentration. (Poly)acrylic acid is a sufficiently strong acid to be appreciably dissociated in the dilute aqueous solutions we have employed, and it may be that the intrinsic attraction to the element at the water-element interface is less for the carboxylate ion species than for the carboxylic acid species.
However, any explanation at this stage would be speculative at best. If further work is to be done, buffered solutions should be employed so that complexities resulting from lack of specificity of the absorbing species will be absent.

New Developments and Progress with CIRIFT Techniques

In the period since completion of our work with surfactant species, several other accounts of applications of the CIRIFT technique have been reported by other groups.

M. Sabo, J. Gross, & I. E. Rosenberg (J. Soc. Cosmet. Chem. 1984, 35, 207-220) have examined other surfactant solutions (sodium lauryl sulfate, ammonium lauryl sulfate, and alpha-olefin sulfates), and A. M.. Dwivedi & D. S. Jayasuiya (Paper PMSE96, 191 st Meeting, American Chemical Society, New York City, April 1986) have studied aqueous solution of poly(ethylene oxide).

In our laboratory, we have successfully incorporated a CIRIFT cell into a Parr stirred reactor system (see accompanying illustration). This offers the potential opportunity to study real-time reactions, including those at elevated temperatures and pressures. The design follows that described by W. R. Moser & E. G. Bartick (SPIE Proceedings, 553, 324-325 (1985)). We suggest that this system offers the opportunity to study many problems of interest to the activities of CANMET both in Ottawa and in Edmonton.

CIRIFT cell incorporated into Parr bomb